
# Phase transition in metal hexammine complexes. II. The EPR spectra of Ni(NO3)26NH3 and Ni++ doped Zn(NO3)26NH3 and Cd(NO3)26NH3

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# Phase transition in metal hexammine complexes. II. The EPR spectra of $Ni(NO_3)_2 6NH_3$ and $Ni^{++}$ doped $Zn(NO_3)_2 6NH_3$ and $Cd(NO_3)_2 6NH_3$

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The cooperative effect of the ammonias in $X(NO_3)_2 6NH_3$ (X = Ni,Zn,Cd) was investigated by EPR. In $Ni(NO_3)_2 6NH_3$, the linewidth of the single EPR absorption line undergoes a sudden broadening at $T_c = 243$ K. This effect is probably a result of a cooperative freezing of the degrees of freedom of rotation of the ammonias, giving the appearance of a crystal field on the $Ni^{++}$ ions. The crystal field does not split the single line, probably because strong exchange effects assemble the lines. The crystal field parameter $D = 0.425$ cm$^{-1}$ was evaluated by applying the Anderson and Weiss theory for the exchange narrowing of the linewidth. Small quantities of the $Ni^{++}$ ions in Zn and Cd salts do not exhibit strong exchange effects. So the single EPR absorption line above $T_c$ goes to a split line below $T_c$. For Ni: $Zn(NO_3)_2 6NH_3$, $T_c = 231$ K and $D = 0.606$ cm$^{-1}$. For Ni: $Cd(NO_3)_2 6NH_3$, $T_c = 198$ K and $D \simeq 0.3$ cm$^{-1}$. Hysteresis in $T_c$ was also observed for all salts.

## INTRODUCTION

In this paper, we report EPR measurements of $Ni^{++}$ in $X(NO_3)_2 6NH_3$ (X = Ni, Zn, and Cd) crystals and attempt to explain the phase transition observed in these salts. In a previous report (I), we have discussed several known properties of these salts and reported the infrared spectra[1] of $Ni(NO_3)_2 6NH_3$ above and below the phase transition ($T_c = 243$ K). The analysis of vibrational data suggests that the origin of this transition is due to the collective freezing of the degrees of rotation of the ammonias.

In the halogen nickel hexammines, $NiY_2 6NH_3$ (Y = Cl, Br, and I), which are isomorphous to the present salts, a single EPR line undergoes a sudden broadening below the critical temperature. For these halogen salts $T_c$ depends on the lattice parameter. Bates and Stevens[2,3] have proposed a model where a crystal field appears at $T_c$, due to a freezing of the rotational degrees of freedom of the ammonias. The effect of this freezing is to remove the zero averaging of the crystal field. This theory was strongly reinforced by observation of the splitting of the single EPR line[4] below $T_c$ for $Ni^{++}$ ions diluted in some nonmagnetic, isomorphous, host salts. This model also predicts that $T_c$ is a function of the lattice parameter.

In this paper, we report that $X(NO_3)_2 6NH_3$ (X = Ni, Zn, Cd) behaves similarly to the halogen nickel hexammine complexes. We also calculate the crystal field parameter $D$, based on linewidth measurements for concentrated $Ni(NO_3)_2 6NH_3$ and for $Ni^{++}$ ions diluted in $X(NO_3)_2 6NH_3$ (X = Zn, Cd). Finally, the Bates and Stevens model is applied for the salts $X(NO_3)_2 6NH_3$ (X = Ni, Zn, Cd).

## SAMPLE PREPARATION

1. $Ni(NO_3)_2 6NH_3$: Reacting $NiCO_3$ (Baker Analysed Reagent) with $HNO_3$ (Reagent PA) and adding concentrated $NH_4OH$ (Berzog PA) in excess to the solution, heat is liberated. During cooling to room temperature, powdered crystals are formed. Octahedral crystals of 2 mm are easily obtained if the powdered crystals are recrystallized slowly at 20 °C maintained by a controlled temperature bath. The crystals were dryed in a desiccator over silica gel in an atmosphere of ammonia. Ammonia analysis by a distillation process (micro Kjeldahl apparatus) indicated the presence of six ammonia molecules per nickel in the samples, within 99% of precision.

2. $Zn(NO_3)_2 6NH_3$ with ~5% $Ni^{++}$ dilution. 5 g of $Zn(NO_3)_2 6H_2O$ (Baker Analysed Reagent) in a Pyrex glass tube were kept in a continuous gas flow of ammonia at 70 °C, maintained by a water bath during 24 h. In this process, most of the water molecules were substituted by ammonia molecules. Then ammonia was liquified in the same tube, using the same gas, by cooling with nitrogen gas obtained from the evaporation of liquid nitrogen contained in a long Dewar. The tube was partially introduced into the Dewar and the desired temperature was achieved by regulating the height of the tube relative to the liquid nitrogen surface. The salt was dissolved in the liquid ammonia, giving a transparent solution. Evaporation of ammonia above – 30 °C carried away the remaining water molecules. Repeating the process of liquefaction and evaporation twice ensured that the samples were free of undesirable water traces. In the final liquefaction, about 0.2 g of $Ni(NO_3)_2 6NH_3$ were added and a faint blue color was observed. The temperature was kept at – 30 °C to assure slow evaporation, and many octahedral crystals were obtained, the largest about 0.5 mm in size. These crystals were carefully transferred to an EPR sample tube at room temperature and 1 atm of ammonia gas. Ammonia analysis and Zn analysis by ignition at 800 °C gave 5.95 ammonia molecules per Zn atom. The crystals of $Zn(NO_3)_2 6NH_3$ are very unstable in air and are highly deliquescent. This is the reason for the special care, as mentioned above, in the crystal

  

preparation. It was not possible to obtain good samples simply by cooling a solution (−10 °C or 0 °C) of the salt in water with excess ammonia.

3. $Cd(NO_3)_2 6NH_3$ with ~5% $Ni^{++}$ doping. This salt was prepared in the same way as the preceding $Zn(NO_3)_2 6NH_3$. The initial salt was $Cd(NO_3)_2 4H_2O$ (Carlo Erba Reagent). If the water elimination process described before is applied, liquid ammonia dissolves the salt, giving a transparent solution as for the Zn salt. The crystals of Cd obtained were larger than the Zn crystals, the largest being about 2 mm. These crystals were more stable than the Zn crystals. Analysis similar to the one made for the Zn salts gives 6.31 ammonia molecules per Cd atom.

## APPARATUS

The EPR spectra of the $Ni(NO_3)_2 6NH_3$ crystals and of the diluted samples were recorded by a Varian 4502-12 X-band spectrometer ($\nu = 9.14$ GHz). Temperature control was performed with a Varian V-4557 variable temperature accessory. Calibration with thermocouple showed an accuracy of ±2 K between 100 K and room temperature.

## EPR SPECTRA OF $Ni(NO_3)_2 6NH_3$

The EPR spectra of the concentrated single crystals of $Ni(NO_3)_2 6NH_3$ show a single absorption line,[5] with behavior quite similar to the one observed for the halogen nickel hexammines.[4,6] Above the transition temperature, an isotropic single line, centered at $g = 2.18$, is observed. Its maximum slope linewidth ($\Delta H_{ms}$) goes from 600 to 500 G as the temperature decreases from room temperature to $T_c$. At 243 K, this line undergoes a sudden broadening to about 2000 G. Figure 1 shows the variation of linewidth ($\Delta H_{ms}$) as a function of temperature.

We verified hysteresis in the transition temperature of about $\Delta T = 5$ K, the effect having been observed previously[7] by a dilatometric technique. The line was fit to the Lorentzian curve within an accuracy of 1%. The $g$ value was the same both above and below $T_c$.

## INTERPRETATION FOR THE $Ni(NO_3)_2 6NH_3$ LINEWIDTH

To explain the observed spectra, we assume that above $T_c$ the $NH_3$ group are rotating, and so the neighborhood of the $Ni^{++}$ ion is a perfectly octahedral environment. Below $T_c$, the loss of this symmetry produced by the freezing of the degrees of freedom of rotation introduces the term $DS_z^2$ to the spin Hamiltonian. That is, a splitting of the single line should be observed below $T_c$. However, in concentrated crystals of $Ni(NO_3)_2 6NH_3$, this splitting was not observed. To explain this, we adopt the assumption that lines are assembled by the exchange interaction.[8]

The dipolar interactions give a linewidth of about $\Delta H^0 = 2$ G, as predicted by Van Vleck's theory,[9] using the $J$ parameter obtained from the Weiss temperature[10] $\theta = 3.3$ K via molecular field theory.

The predicted value of $\Delta H^0 = 2$ G above $T_c$ is much lower than the experimental value $\Delta H^n = 430$. This large discrepancy between the dipolar and the experimental broadening suggests that we have many unknown sources of line broadening. That is,

$$\Delta H^n = \Delta H^0 + \Delta H^u ,$$

where $\Delta H^u$ is from unknown sources of broadening and is supposed to be independent from the exchange interaction. If a crystal field contribution is included, we have

$$\Delta H = [(H_p^0)^2 + (H_p^D)^2]/H_e + \Delta H^u$$

or

$$\Delta H^D = \Delta H - \Delta H^n = (H_p^D)^2/H_e .$$

That is, for the purpose of the linewidth analysis below $T_c$, we have to subtract 430 G to obtain that part of the width due to the phase transition effect.

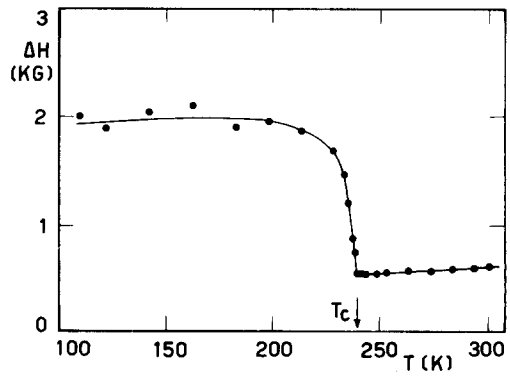


FIG. 1. The EPR maximum slope linewidth, $\Delta H_{ms}$, vs temperature of the $Ni(NO_3)_2 6NH_3$.

Below $T_c$, we have to introduce the crystal field. We can write the crystal field Hamiltonian by

$$\hat{H}_D = D \sum_i (\mathbf{S}_i \cdot \mathbf{n}_i)^2 ,$$

where $\mathbf{n}_i$ is the direction of the distortion in the unit cell. The second moment is given by

$$(\omega_p^D)^2 = \frac{1}{\hbar^2} \frac{T_r\{[\hat{H}_D, [\hat{H}_D, S^-]]S^+\}}{T_r[S^-, S^+]} ,$$

where $S^{\pm} = S_x \pm iS_y$, and $D$ is the cubic crystal field parameter. Assuming the distortion in the direction (111), we obtain

$$(\omega_p^D)^2 = \frac{10}{3}\frac{D^2}{5\hbar^2} \quad \text{or} \quad (H_p^D)^2 = \frac{2}{3}\left(\frac{D}{g\beta}\right)^2 .$$

Then we have

$$\Delta H^D = \tfrac{2}{3}(D/g\beta)^2/H_e .$$

By using the experimentally observed $\Delta H$ reduced by 430 K to account for the unknown sources of broadening, we have

$$D = 0.425 \text{ cm}^{-1} .$$

## EPR SPECTRA OF $Ni:Zn(NO_3)_2 6NH_3$

$Zn(NO_3)_2 6NH_3$ is expected to be quite similar to $Ni(NO_3)_2 6NH_3$ because the $Ni^{++}$ and $Zn^{++}$ ions are

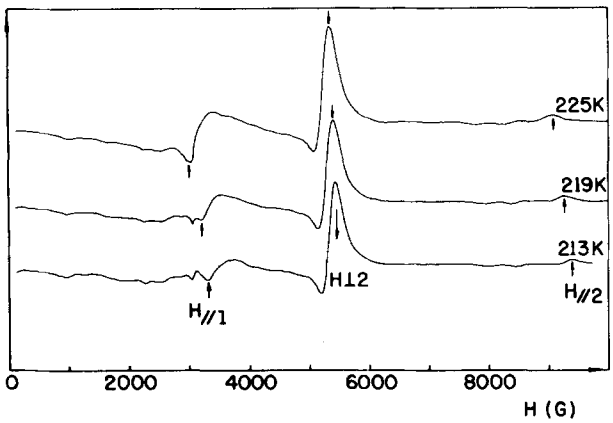


FIG. 2. The EPR spectra of the Ni: $Zn(NO_3)_2 6NH_3$.

expected to have almost the same radius. However, we do not have measurements of the lattice parameter of the Zn salt. Above $T_c$, the Ni diluted in the Zn salt shows an isotropic single line with $\Delta H = 430$ G, like the one observed in the concentrated salt, although we now have crystals mixed with powder. $T_c$ is 231 K, which is 12 K below the transition temperature for the Ni salt. Hysteresis in $T_c$ was about 5 K, as for the Ni salt. Below $T_c$, the single line splits into several lines. The characteristic features of the lines below $T_c$ are shown in Fig. 2.

For the spectra interpretation, we use the method due to Wasserman *et al.*[11] As the number of lines is greater than expected for the powdered samples, we adopt as primary assignment the strong absorption line at 5250 G. The Hamiltonian is assumed to be

$$\hat{H} = g\beta \mathbf{H} \cdot \mathbf{S} + DS_z^2 .$$

The intense asymmetrical line at 5250 G was assigned as $H_{\perp 2}$ and so we must have $h\nu < D$. If this assignment is assumed, there are two other lines with small intensity and assigned to $H_{\parallel 1}$ and $H_{\parallel 2}$ transitions. Experimentally, these lines were observed at 3000 and 9050 G and have small intensities.

At 225 K, we have

$$g = 2.17 ,$$

$$D = 0.606 \text{ cm}^{-1} ,$$

in good agreement with values given for undiluted $Ni(NO_3)_2 6NH_3$.

The number of lines present in the observed spectra is greater than the set of three lines mentioned above. The extra lines are probably due to magnetic impurities, such as Co, Fe, and others. But to assure our assignment, we also discuss the temperature behavior of the spectra. When the temperature was lowered, we observed that a number of lines moved slowly to higher magnetic fields, suggesting that $D$ increases as the temperature decreases. For $h\nu < D$, if $D$ increases, the values of the fields of the lines assigned to $H_{\parallel 1}$, $H_{\parallel 2}$, and $H_{\perp 2}$ must increase, as was observed (see Fig. 2).

## EPR SPECTRA OF $Ni:Cd(NO_3)_2 6NH_3$

The EPR spectra of $Ni:Cd(NO_3)_2 6NH_3$ is different from that observed for $Ni:Zn(NO_3)_2 6NH_3$. The values of $T_c$ are also different, with $T_c = 231$ K for Ni: Zn salt and $T_c = 198$ K for Ni: Cd. The single line at $g = 2.17$ breaks down at $T_c$ and several lines appear and the behavior of the spectra of these salts is different, as can be seen by comparing Figs. 2 and 3. A very weak line at 6000 G and a broad line near $H = 0$ indicates that $D \simeq h\nu$. By assigning the 6000 G line to $H_{\parallel 2}$, we have

$$D \simeq 0.3 \text{ cm}^{-1} .$$

The hysteresis is about 10 K, two times larger than the one observed for $Ni(NO_3)_2 6NH_3$ and $Ni:Zn(NO_3)_2 6NH_3$. The value of $D$ in the Ni: Zn salt is greater than in the Ni: Cd salt. This observation cannot yet be explained from the present available experimental data.

## DISCUSSION

The observation that the linewidth $\Delta H^n$ is the same in both undiluted and doped salts of $Ni(NO_3)_2 6NH_3$ above $T_c$ indicates that $\Delta H^n$ is the natural linewidth arising from unknown sources of broadening. The dipolar contribution to the linewidth was shown to be negligible. The value used in the evaluation of the dipolar contribution $H_e = 10\,400$ G is in good agreement with the experimentally observed exchange field of about 13 000 G.[12]

The sudden broadening of the line in the undiluted salt and the splitting of the single isotropic line in the doped salts at $T_c$ were interpreted as due to the appearance of an observable crystal field. This supports the hypothesis of the collective freezing of degrees of freedom of the ammonias in the skeleton $|X(6NH_3)|^{++}$.

The values of $D$ were assigned as

| | |
|---|---|
| $D = (0.425 \pm 0.003)$ cm$^{-1}$ | $Ni(NO_3)_2 6NH_3$ , |
| $D = (0.606 \pm 0.003)$ cm$^{-1}$ | $Ni:Zn(NO_3)_2 6NH_3$ , |
| $D \simeq 0.3$ cm$^{-1}$ | $Ni:Cd(NO_3)_2 6NH_3$ . |

The mean value of $D$ for the diluted salts, $D = 0.45$ cm$^{-1}$, is in good agreement with the value obtained from linewidth data.

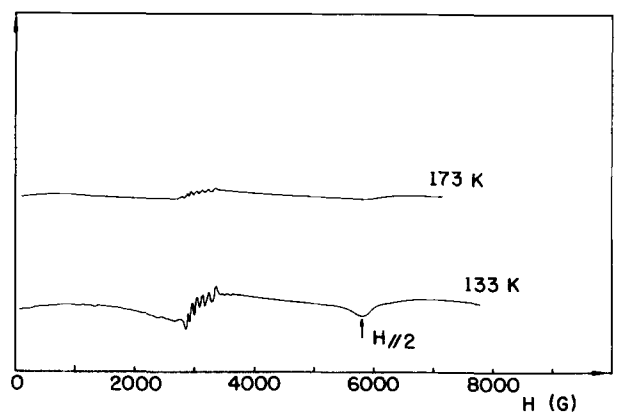


FIG. 3. The EPR spectra of the Ni: $Cd(NO_3)_2 6NH_3$.

The values of $T_c$ were observed to be

$T_c = 243$ K $\quad Ni(NO_3)_2 6NH_3$ ,

$T_c = 231$ K $\quad Ni : Zn(NO_3)_2 6NH_3$ ,

$T_c = 198$ K $\quad Ni : Cd(NO_3)_2 6NH_3$ ,

that is, $T_c(Ni) > T_c(Zn) > T_c(Cd)$.

The present observed behavior for the linewidth is very similar to the one observed for the halogen hexammine salts. The Bates and Stevens model, developed for the halide salts, fails when applied to nitrate salts. The lattice parameter of $Ni(NO_3)_2 6NH_3$ is $a = 10.96$ Å, which is between the lattice parameters of $NiBr_2 6NH_3$ ($a = 10.46$ Å) and $NiI_2 6NH_3$ ($a = 11.01$ Å).

Thus, we might expect that the transition temperature of $Ni(NO_3)_2 6NH_3$ will be between the $T_c$'s of these salts, i.e., between 45 K and 24 K. But for $Ni(NO_3)_2 6NH_3$, we have $T_c = 243$ K larger than the expected. This high value of $T_c$ was discussed previously[1] and attributed to the contribution of an extra potential on the hydrogens of the $NH_3$ by the nitrate radicals. Including the effect of the nitrate radical in the Bates and Stevens model, it is possible to predict that $T_c$ increases as the lattice parameter decreases in the $X(NO_3)_2 6NH_3$ salts.

The lattice parameters of Zn and Cd salts are unknown. The lattice parameter of the Zn salt is expected to be slightly greater than the lattice parameter of the Ni salt, because Zn has a larger atomic radius than Ni. In the same way, we expect the parameter of the Cd salt to be the largest one, that is

$$a(Ni) < a(Zn) < a(Cd) .$$

This correlation between the lattice parameters gives

$$T_c(Ni) > T_c(Zn) > T_c(Cd)$$

by using the Bates and Stevens modified model. This is now in agreement with the experimentally observed correlation. It may be assumed that this procedure is correct, since we are comparing crystals assumed to be of the same structure.

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[1] S. Isotani, W. Sano, and J. A., Ochi, "Phase Transition in Metal Hexammine Complexes. I-Infrared Spectra of $Ni(NO_3)_2 6NH_3$," (accepted for publication) J. Phys. Chem. Solids.
[2] A. R. Bates, and K. W. H. Stevens, J. Phys. C 2, 1573 (1969).
[3] A. R. Bates, J. Phys. C 3, 1825 (1970).
[4] C. Trapp, and C. I. Shyr, J. Chem. Phys. 54, 196 (1971).
[5] C. E. Hennies, Ph. D. thesis, Faculdade de Filosofia, Ciências e Letras da Universidade de São Paulo, 1969 (unpublished).
[6] M. B. Palma-Vittorelli, M. V. Palma, G. W. J. Drewes, and W. Koerts, Physica (Utr.) 26, 922 (1960).
[7] D. G. Thomas, L. A. K. Staveley, and A. F. Cullis, J. Chem. Soc. 1952, 1727.
[8] P. W. Anderson, and P. R. Weiss, Rev. Mod. Phys. 25, 269 (1953).
[9] J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).
[10] C. C. Becerra, W. Sano, A. Marques, G. Frossatti, A. Paduan F°, N. F. Oliveira Jr., and C. J. A. Quadros, Phys. Lett. A 40, 203 (1972).
[11] E. Wasserman, L. C. Snyder, and W. A. Yager, J. Chem. Phys. 41, 1763 (1964).
[12] A. Paduan F°, "Magnetic Phase Diagram of $Ni(NO_3)_2 6NH_3$ by Magnetic Susceptibility Measurements," Ph. D. thesis, Faculdade de Filosofia, Ciências e Letras de Rio Claro, 1973 (unpublished).